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(54) Steam reforming purified hydrocarbon gas streams

(57) A reformed gas stream is produced from a gaseous hydrocarbon feedstock stream containing both carbon dioxide and sulphur compounds, by subjecting the feedstock stream to a membrane separation process thereby producing a permeate stream containing at least part of the carbon dioxide and sulphur compounds, combusting the permeate stream and recovering energy from the combustion products, subjecting the impermeate stream to desulphurisation by passage over a bed of a particulate absorbent for hydrogen sulphide, thereby producing a desulphurised impermeate stream, adding steam to said impermeate stream, and subjecting the mixture of steam and said desulphurised impermeate stream to steam reforming over a steam reforming catalyst. The permeate stream may be used as fuel for the reforming, which latter may be a two-stage process.

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### Reforming

This invention relates to reforming and in particular to the steam reforming of gaseous hydrocarbon feedstocks such as natural gas. This process is often employed in the production of hydrogen-containing gas streams, for example relatively pure hydrogen for use in eg hydrogenation reactions, synthesis gas for the production of organic compounds such as methanol and higher alcohols, or synthesis gas for the production of ammonia.

In a steam reforming process a feedstock and steam are passed over a steam reforming catalyst, generally disposed in externally heated tubes. The catalysts employed in such a process generally comprise nickel on a suitable refractory support such as alumina or calcium aluminate cement. Such nickel catalysts are poisoned by sulphur compounds and, since sulphur compounds are often present in gaseous hydrocarbon feedstocks such as natural gas, it is conventional practice to remove the sulphur compounds prior to reforming.

The method employed for removing the sulphur compounds will depend on the nature and proportions of the sulphur compounds. For feedstocks containing relatively small proportions of sulphur compounds, eg below about 100 ppm, preferably below 30 ppm, by volume of sulphur expressed as equivalent hydrogen sulphide, absorption of the hydrogen sulphide by a particulate absorbent such as zinc oxide is satisfactory. Prior to absorption, the feedstock is often subjected to hydrodesulphurisation, wherein the feedstock, plus a small proportion of hydrogen, is passed over a hydrodesulphurisation catalyst, typically nickel or cobalt molybdate, to convert organic sulphur compounds such as mercaptans to hydrogen sulphide.

For larger quantities of sulphur compounds, absorption using a regenerable liquid absorbent, or an iron sponge, may be employed. However such process involve significant additional capital and/or operating costs, and also present effluent disposal problems.

The product of the reforming reaction contains hydrogen, carbon oxides, steam, and methane. For many applications, the reforming operation is effected in two stages, primary reforming where as described above the catalyst is disposed in externally heated tubes and secondary reforming wherein air or oxygen is added to the primary reformed gas and the mixture subjected to partial combustion before passing adiabatically over a secondary reforming catalyst. In such a two stage process employing air, the product will also contain nitrogen.

Subsequent processing of the reformed gas will depend on the intended use. Often, especially for the manufacture of ammonia synthesis gas or hydrogen, the reformed gas is subjected to one or more stages of the shift reaction with steam to convert carbon monoxide to carbon dioxide and hydrogen. It is then often necessary to remove residual steam and the carbon dioxide. Steam may readily be removed by cooling the gas to below the dew point of steam to condense the steam as a liquid water phase which can be

separated. The carbon dioxide is often removed by absorption into a suitable absorbent liquid or by a pressure swing adsorption process.

The gaseous hydrocarbon feedstock often contains appreciable quantities of carbon dioxide. While carbon dioxide can at least partially replace steam in the reforming reaction, in processes wherein the carbon dioxide is removed from the reformed gas, eg after one or more shift stages, it is seen that any carbon dioxide in the feedstock acts essentially as a diluent, decreasing the amount of hydrocarbon that can be processed in a given plant, and providing an additional load on the carbon dioxide removal stage. In such cases it would be desirable to remove some or all of the carbon dioxide from the feedstock prior to reforming, but the economic advantages of so doing have to be balanced against the additional cost of this carbon dioxide removal stage.

The hydrocarbon feedstock may also contain other unwanted components such as helium or nitrogen. We have realised that at least some of the carbon dioxide in the feedstock, together with helium (if present), and, in some cases also nitrogen (if present), can be separated together with at least some of the sulphur compounds by a simple technique which renders subsequent desulphurisation with a particulate absorbent more economic. In the present invention a membrane system is employed to effect this initial separation.

The use of membrane systems to separate carbon dioxide from hydrocarbon feedstocks is well known, for example see the paper by Bilstad et al entitled "CO<sub>2</sub>/HC membrane separation: a mature technology", presented at the AIChE Symposium for Membrane Separation for Gas Processing at New Orleans on March 29-April 2, 1992. By the use of such a membrane system, a permeate stream containing carbon dioxide, hydrogen sulphide, and helium (if present) and possibly, depending on the nature of the membrane, also organic sulphur compounds and/or nitrogen, can be separated from the non-permeate hydrocarbon stream. Inevitably the permeate will contain, in addition to hydrogen sulphide, some other combustible materials: thus if a hydrosulphurisation step precedes the membrane separation, the permeate will also contain some hydrogen. In the present invention the permeate stream is used as fuel.

Accordingly the present invention provides a process for the production of a reformed gas stream from a gaseous hydrocarbon feedstock stream containing both carbon dioxide and sulphur compounds, comprising subjecting said feedstock stream to a membrane separation process thereby producing a permeate stream containing at least part of the carbon dioxide and sulphur compounds, combusting the permeate stream and recovering energy from the combustion products, subjecting the impermeate stream to desulphurisation by passage over a bed of a particulate absorbent for hydrogen sulphide, thereby producing a desulphurised impermeate stream, adding steam to said impermeate

stream, and subjecting the mixture of steam and said desulphurised impermeate stream to steam reforming over a steam reforming catalyst.

Preferably the process gas is subjected to a hydrodesulphurisation step wherein a hydrogen-containing gas is added and the mixture passed over a hydrodesulphurisation catalyst to convert organic sulphur compounds to hydrogen sulphide, before the impermeate is passed over the hydrogen sulphide absorbent. Such a hydrodesulphurisation step may be effected before or after the membrane separation step. Since hydrogen will usually permeate the membrane employed, if the hydrodesulphurisation stage is effected after the membrane separation stage, it is necessary to add the hydrogen-containing stream to the impermeate after the membrane separation stage. Preferably the hydrodesulphurisation step is effected prior to the membrane separation stage: this has the advantage that organic sulphur compounds will be converted to hydrogen sulphide before the membrane separation step and so will be separated as the permeate stream. Not only does this reduce the load on the particulate absorbent, but also residual hydrogen will form part of the permeate and so add to the fuel value of the permeate. Also this means that membranes that do not pass the organic sulphur compounds can advantageously be employed: while membranes that do not pass the organic sulphur compounds could be employed even where the hydrodesulphurisation is effected after membrane separation, the fuel value resulting from these compounds is lost and also a greater burden is placed upon the subsequent particulate absorbent.

Membranes that may be employed are generally polymeric materials such as polysulphones, cellulose acetate, polyimides, polycarbonates, polyamides, polyetherimides and sulphonated polysulphones. The temperature at which the membrane separation step is operated will normally be limited by the nature of the membrane: preferably the temperature is below about 90°C. The pressure of the feed to the membrane separation step will normally be determined by the pressure employed in the subsequent reforming step, which will usually be in the range 10 to 45 bar abs.

It will be appreciated that since carbon dioxide will be produced in the subsequent reforming stage, the impermeate is subjected to desulphurisation prior to reforming, and the permeate is used as fuel, it is not necessary that the membrane system is particularly selective. Thus the membrane separation stage is employed simply to remove some of the carbon dioxide and sulphur compounds in the feedstock and it does not matter if some of the hydrocarbon also permeates the membrane. Consequently the membrane separation stage may be kept simple and only a single membrane stage need be employed, although more complex systems, eg employing two or more membrane separation stages may be used if desired.

In the present invention the permeate stream is combusted and energy recovered therefrom. For example, and preferably, the permeate stream is used as fuel in

the reforming stage, particularly where at least part of the reforming is effected by passing the mixture of desulphurised feedstock and steam over a reforming catalyst disposed in tubes heated by combustion of a fuel. Additional fuel, eg a part stream taken from the original feedstock before membrane separation, may be used to supplement the permeate stream. Alternatively, or additionally, a fuel from another source may be used to supplement the permeate stream if required. In a typical ammonia plant, purge gas taken from the ammonia synthesis loop may be used as such supplemental fuel. Alternatively the permeate may be combusted and heat recovered from the combustion products by heat exchange with reactants, eg the desulphurised feedstock, steam, and/or air or oxygen (if used), fed to the reforming step, or by heat exchange with a stream employed in the further processing of the reformed gas. In another alternative, the permeate may be combusted, eg in a gas turbine, and energy recovered from the combustion products by expansion in a turbine driving a pump or compressor compressing the reformed gas, or a gas, eg synthesis gas, produced therefrom and/or one or more of the reactants used in the reforming step or in the subsequent processing of the reformed gas. Since the permeate contains a significant proportion of carbon dioxide, it may be desirable to effect the combustion thereof catalytically, but it will be appreciated that in this case it will be necessary to employ a combustion catalyst that is not poisoned by sulphur compounds.

In many plants, purge streams etc. to be used as fuel are mixed, optionally also with additional fuel, to form a fuel "pool" which is then employed to fuel the reformer, fired heaters, gas turbines driving pumps and compressors etc. In the present invention, the permeate stream may form part of this fuel "pool".

The particulate absorbent may be any of those conventionally employed for desulphurisation, and will normally comprise one or more metals, or compounds thereof, selected from zinc, copper, nickel, iron, manganese, tin, lead, and silver. Other metals or compounds thereof may also be present. The particulate absorbent preferable comprises zinc compounds, such as zinc oxide, zinc carbonate, zinc hydroxycarbonate, and mixtures thereof, alone or in conjunction with other metals or compounds thereof, such as copper, copper oxide, copper carbonate, basic copper carbonate, alumina and/or calcium aluminate.

For efficient operation, it is preferred that the membrane system removes such an amount of sulphur compounds into the permeate stream that the impermeate stream has a sulphur content, expressed as equivalent hydrogen sulphide, of below about 10 ppm by volume. The temperature employed for desulphurisation will depend on the absorbent employed and typically will be in the range 0 to 400°C.

In some cases for efficient reforming it is desirable to subject the desulphurised feedstock to a pre-reforming step wherein the desulphurised feedstock and steam are preheated and then passed adiabatically through a bed of a reforming catalyst active at low reforming temperatures and then the resultant pre-reformed product is subjected to

reforming in an externally heated tube reformer. For such a pre-reforming step a catalyst having a relatively high nickel content, typically above 50% by weight, is desirable and these are particularly susceptible to poisoning by sulphur compounds. In such a process it may therefore be desirable to subject the desulphurised gas from a zinc based absorbent to a further polishing desulphurisation stage using a bed of a particulate absorbent material containing both copper and zinc compounds. A suitable copper/zinc absorbent material is described in EP-A-243052.

The invention is of particular utility where the hydrocarbon feedstock is natural gas containing at least about 5%, preferably at least about 10%, by volume of carbon dioxide and the membrane system removes such an amount of carbon dioxide that the impermeate has a carbon dioxide content below about 4% by volume.

The reforming conditions, eg steam to hydrocarbon carbon ratio, pressure, catalyst outlet temperature, space velocity etc., may be those conventionally used in the art. A secondary reforming step may follow primary reforming if required (as is usually the case for the production of ammonia synthesis gas).

The invention is illustrated by the following calculated example of the use of the process to supply reformed gas suitable for the production of 1554 metric tons of ammonia per day.

2700 kmol/h of natural gas of the following approximate composition (% by volume):

methane	77
ethane	6
propane	1
carbon dioxide	16

and containing about 80 ppm by volume of hydrogen sulphide was fed to a membrane separation unit at a pressure of 30 bar abs. and a temperature of 45°C to give 1065 kmol/h of a permeate at 6 bar abs. of approximate composition (% by volume):

methane	61
ethane	3.5
propane	0.1
carbon dioxide	35.3

and containing about 172 ppm by volume of hydrogen sulphide and 1635 kmol/h of an impermeate at 29.5 bar abs. of the approximate composition (% by volume):

methane	87.5
ethane	7.5
propane	1.6
carbon dioxide	3.4

and containing about 20 ppm by volume of hydrogen sulphide.

The hydrogen sulphide was separated from the impermeate using a zinc oxide absorbent material, steam was added at a rate of 5628 kmol/h and the resultant mixture was subjected to primary steam reforming in externally heated tubes over a steam reforming catalyst comprising nickel on a calcium aluminate support at an exit temperature of 792°C.

- 5 The primary reformed gas was then subjected to secondary reforming with the addition of air at a rate of 2464 kmol/h to give an outlet temperature of 916°C. The secondary reformed gas was then cooled and subjected to high temperature shift and then low temperature shift to give a shifted gas at a rate of 12678 kmol/h (wet gas) containing about 14% by volume carbon dioxide, 45% by volume hydrogen and 15% by volume of nitrogen.
- 10 Part of the permeate (850 kmol/h) was used as the fuel to heat the primary reformer while the remainder of the permeate was added to the ammonia plant fuel pool for combustion for other heating purposes.

**Claims**

1. A process for the production of a reformed gas stream from a gaseous hydrocarbon feedstock stream containing both carbon dioxide and sulphur compounds, comprising subjecting said feedstock stream to a membrane separation process thereby producing a permeate stream containing at least part of the carbon dioxide and sulphur compounds, combusting the permeate stream and recovering energy from the combustion products, subjecting the impermeate stream to desulphurisation by passage over a bed of a particulate absorbent for hydrogen sulphide, thereby producing a desulphurised impermeate stream, adding steam to said impermeate stream, and subjecting the mixture of steam and said desulphurised impermeate stream to steam reforming over a steam reforming catalyst.
2. A process according to claim 1 wherein, before the membrane separation step, the feedstock stream is subjected to a hydrodesulphurisation step wherein a hydrogen-containing gas is added and the mixture passed over a hydrodesulphurisation catalyst to convert organic sulphur compounds to hydrogen sulphide.
3. A process according to claim 1 wherein a hydrogen-containing stream is added to the impermeate stream and the mixture passed over a hydrodesulphurisation catalyst to convert organic sulphur compounds to hydrogen sulphide before the impermeate stream is passed over the hydrogen sulphide absorbent.
4. A process according to any one of claims 1 to 3 wherein the membrane separation step is effected at a temperature below 90°C.
5. A process according to any one of claims 1 to 4 wherein the permeate stream is used as fuel in the reforming step.
6. A process according to any one of claims 1 to 5 wherein the particulate absorbent comprises at least one zinc compound selected from zinc oxide, zinc carbonate, and zinc hydroxycarbonate, alone or in conjunction with at least one material selected from copper, copper oxide, copper carbonate, basic copper carbonate, alumina, and calcium aluminate.
7. A process according to any one of claims 1 to 6 wherein the desulphurised impermeate stream is subjected to a pre-reforming step wherein the desulphurised



- impermeate stream and steam are preheated and then passed adiabatically through a bed of a reforming catalyst active at low reforming temperatures and then the resultant pre-reformed product is subjected to reforming in an externally heated tube reformer.
8. A process according to claim 7 wherein a catalyst having a high nickel content is used for the pre-reforming step, the particulate absorbent comprises at least one zinc compound, and the desulphurised gas from that particulate absorbent is subjected to a further step of desulphurisation using a bed of a particulate absorbent material containing both copper and zinc compounds.
  9. A process according to any one of claims 1 to 8 wherein the hydrocarbon feedstock is natural gas containing at least about 5% by volume of carbon dioxide and the membrane system removes such an amount of carbon dioxide that the impermeate has a carbon dioxide content below about 4% by volume.
  10. A process for the production of ammonia synthesis gas comprising producing a reformed gas stream by a process according to any one of claims 1 to 9 wherein the reforming operation is effected by primary reforming using a catalyst disposed in externally heated tubes and secondary reforming wherein air is added to the primary reformed gas and the mixture subjected to partial combustion before passing adiabatically over a secondary reforming catalyst, and then the reformed gas is subjected to one or more stages of the shift reaction with steam to convert carbon monoxide to carbon dioxide and hydrogen, and thereafter carbon dioxide is removed.

<b>Patents Act 1977</b> <b>Examiner's report to the Comptroller under Section 17</b> 9 <b>(The Search report)</b>	<b>Application number</b> <b>GB 9414727.9</b>
<b>Relevant Technical Fields</b>  (i) UK Cl (Ed.M)      C5E (EPA, EPC, EPG, EPQ) (ii) Int Cl (Ed.5)      C01B (3/02, 38, 40, 42, 44)  <b>Databases (see below)</b> (i) UK Patent Office collections of GB, EP, WO and US patent specifications.  (ii) WPI, CLAIMS	<b>Search Examiner</b> <b>R E HARDY</b>
	<b>Date of completion of Search</b> <b>25 OCTOBER 1994</b>
	<b>Documents considered relevant following a search in respect of Claims :-</b> <b>ALL</b>

**Categories of documents**

<b>X:</b> Document indicating lack of novelty or of inventive step.	<b>P:</b> Document published on or after the declared priority date but before the filing date of the present application.
<b>Y:</b> Document indicating lack of inventive step if combined with one or more other documents of the same category.	<b>E:</b> Patent document published on or after, but with priority date earlier than, the filing date of the present application.
<b>A:</b> Document indicating technological background and/or state of the art.	<b>&amp;:</b> Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
A	GB 2194958 A (HUMPHREYS & GLASGOW)	1
A	GB 1478083 A (INST OF GAS TECHNOLOGY)	1
A	EP 0099868 A1 (MONSANTO)	1
A	WPI Abstract Accession No 93-080648/10 & JP 05025482 A 02.02.93 MITSUBISHI - see Abstract	1

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